

Magnetoelastic effects in multiferroic YMnO₃

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We have investigated magnetoelastic effects in multiferroic YMnO₃ below the antiferromagnetic phase transition, $T_N \approx 70$ K, using neutron powder diffraction. The a lattice parameter of the hexagonal unit cell of YMnO₃ decreases normally above T_N , but decreases anomalously below T_N , whereas the c lattice parameter increases with decreasing temperature and then increases anomalously below T_N . The unit cell volume also undergoes an anomalous contraction below T_N . By fitting the background thermal expansion for a non-magnetic lattice with the Einstein-Grüneisen equation, we determined the lattice strains Δa , Δc and ΔV due to the magnetoelastic effects as a function of temperature. We have also determined the temperature variation of the ordered magnetic moment of the Mn ion by fitting the measured Bragg intensities of the nuclear and magnetic reflections with the known crystal and magnetic structure models and have established that the lattice strain due to the magnetoelastic effect in YMnO₃ couples with the square of the ordered magnetic moment or the square of the order parameter of the antiferromagnetic phase transition.

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I. INTRODUCTION

The coupling between spin and lattice degrees of freedom is one of the interesting topics of condensed matter research^{1–11}. It has drawn renewed interest in connection with potentially useful electronic materials, such as colossal magnetoresistive and multiferroic materials. One of the most dominant effects of this coupling is the spontaneous exchange striction associated with the magnetic ordering at lower temperatures. If the material does not contain any magnetic ions, the temperature variation of the volume is smooth and shows no anomalies at low temperatures. However, if the material contains magnetic ions that order at low temperature, then at this transition temperature the positions of the atoms may be modified. The most easily probed effects are the modifications of the unit cell parameters and the unit cell volume. Sometimes the lattice symmetry may get modified following the symmetry of the magnetically ordered state. The symmetry change at the ordering temperatures also causes crystallographic and/or magnetic domains to be formed in single crystal samples. In addition to the lattice strain effects, important modifications in the positional parameters of the atoms and also in the bond distances may take place. However, these modifications are more difficult to detect because the effects are small. To effectively measure this, one needs the temperature variation of the diffraction intensities and, preferably, the diffuse scattering up to high momentum transfer of the scattered radiation. A particularly complex situation arises for magnetic structures with the propagation vector $\mathbf{k} = 0$. In this case, the magnetic reflections occur at the same position as the nuclear reflections and the refinement of the magnetic and crystal structures become fraught with great difficulties.

YMnO₃ belongs to the family of hexagonal manganites RmO₃ (R = Sc, Y, Er, Ho, Tm, Yb, Lu) that show multiferroic behaviour¹². These hexagonal manganites are paraelectric at high temperatures with the centrosymmetric space group $P6_3/mmc$. Below about 1000 K they undergo a paraelectric-to-ferroelectric transition to the non-centrosymmetric structure with the space group $P6_3cm$. Fig. 1 shows schematically the crystal structure of YMnO₃ in the ferroelectric phase. At lower temperatures, of the order of about 100 K, the magnetic hexagonal manganites order with a non-collinear antiferromagnetic structure with a propagation vector $\mathbf{k} = 0$. Among these hexagonal manganites YMnO₃ and HoMnO₃ have been investigated quite intensively^{12–18}. Here we report the powder neutron diffraction investigation of the temperature dependence of the crystal and magnetic structure of YMnO₃. We have observed strong magnetoelastic effects or spontaneous magnetostriction below the Néel temperature $T_N \approx 70$ K. The lattice strains are found to be proportional to the square of the ordered magnetic moments of the Mn ions.

In order to determine quantitatively the magnetoelastic effect or the spontaneous magnetostriction, we need to measure the temperature variation of the lattice parameters and the unit cell volume. The high temperature data above the ordering temperature can be fitted to either a Debye model, using the Grüneisen approximation,¹⁹ or the simpler Einstein model and then extrapolated to lower temperatures to give the background variations in the absence of magnetism. The simpler Einstein-Grüneisen equation serves as an excellent fit function for not only the volume but also for the individual lattice parameters²⁰ and we have used it here.

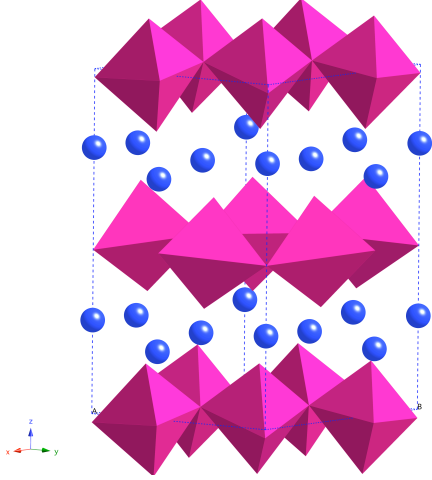


FIG. 1: (Color online) Schematic representation of the crystal structure of YMnO_3 . The red polyhedra represent MnO_5 bipyramids and the blue spheres represent the Y ions.

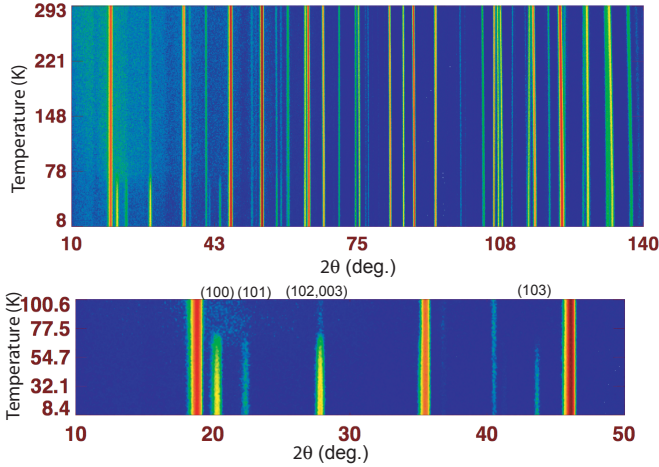


FIG. 2: (Color online) (Upper panel) Temperature variation of the diffraction intensities of YMnO_3 . (Lower panel) The same plot in a limited low 2θ range showing the temperature variation of the peaks with dominant magnetic contribution.

II. EXPERIMENTAL METHODS

Neutron diffraction experiments were done on YMnO_3 on the high intensity powder diffractometer²¹ D20 of the Institute Laue-Langevin in Grenoble. The 115 reflection

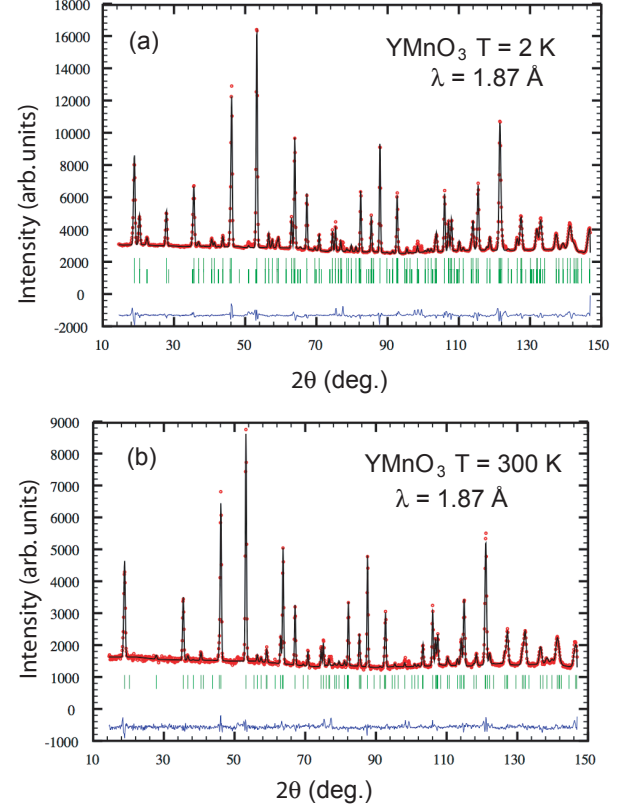


FIG. 3: (Color online) Rietveld refinement of the (a) crystal and magnetic structures of YMnO_3 at $T = 2$ K and (b) the crystal structure of YMnO_3 at $T = 300$ K. The ticks in (a) give the positions of the nuclear and magnetic Bragg peaks whereas those in (b) give the positions of the nuclear peaks only.

from a Ge monochromator at a high take-off angle of 118° gave a neutron wavelength of 1.868 \AA . Approximately 3 g of powdered YMnO_3 was placed inside an 8 mm diameter vanadium can, which was fixed to the sample stick of a standard ^4He cryostat.

III. RESULTS

We measured the diffraction intensities from YMnO_3 as a temperature in the range $2 - 300$ K. The upper panel of Fig. 2 shows the temperature variation of the diffraction intensities of YMnO_3 whereas the lower panel shows a similar plot in a limited low 2θ range showing the temperature variation of the peaks with a dominant magnetic contribution. The magnetic contributions to the intensity are clearly seen in the plot of the lower panel. The reflections like $h0l$ with $l = \text{odd}$ disappear completely at T_N as they are forbidden reflections in the space group $P6_3cm$ and have only magnetic contribution and therefore become zero at T_N . The other reflections

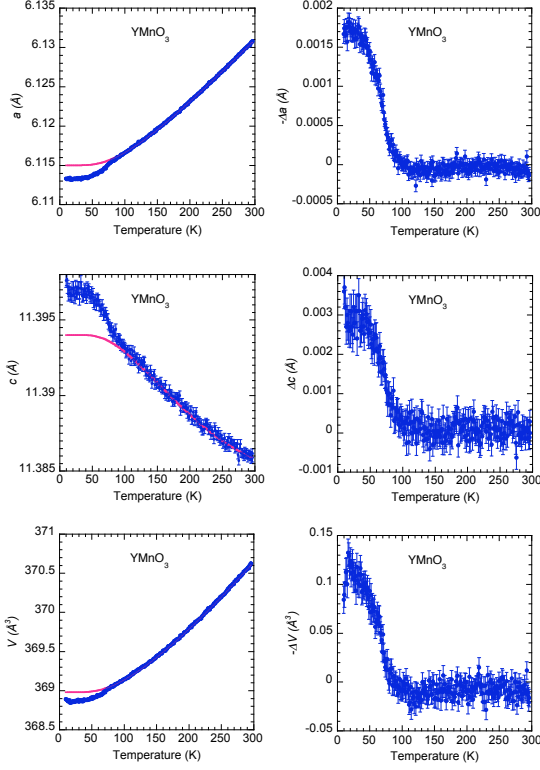


FIG. 4: (Color online) Temperature variation of the lattice parameters a , c , and the unit cell volume V of YMnO_3 plotted on the left panel. The red curves in these figures represent the lattice parameter and the unit cell volume obtained by fitting the high temperature data by the Einstein-Grüneisen equation and extrapolated to low temperature to give the background for the non-magnetic lattice. On the right panel the temperature dependence of the lattice strains Δa , Δc and ΔV obtained by subtracting the non-magnetic background have been plotted.

that have both magnetic and nuclear contributions attain a constant value (nuclear) above T_N . The Rietveld refinement²² of the diffraction data was done using the Fullprof program²³. The refinement results from YMnO_3 at $T = 2$ K and 300 K are shown in Fig. 3. At $T = 2$ K, the intensity data have been fitted with the crystal and the magnetic structure model¹⁶ of YMnO_3 . At $T = 300$ K, in the paramagnetic state, the refinement was done with the crystal structure model only.

Figure 4 shows the temperature variation of the lattice parameters a , c , and the unit cell volume V of YMnO_3 plotted on the left panel. The lattice parameter a decreases continuously with decreasing temperature but, close to the Néel temperature $T_N \approx 70$ K, shows a magnetoelastic or magnetostriction anomaly. The red curve

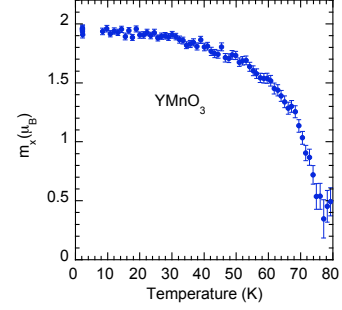


FIG. 5: (Color online) Temperature variation of the ordered x -component of magnetic moment m_x of the Mn ion obtained by fitting the measured Bragg intensities of the nuclear and magnetic reflections with the known crystal and magnetic structure models.

represents the background variation of the a lattice parameter for a non-magnetic solid obtained by fitting the data in the paramagnetic state by the Einstein-Grüneisen equation. By subtracting the background from the data we determined the lattice strain Δa , plotted on the right panel of Figure 4. The c lattice parameter increases continuously with decreasing temperature down to T_N and then shows an anomalous increase or positive magnetostriction. By subtracting the background variation of the c lattice parameter (red continuous curve) from the data we determined the lattice strain Δc plotted on the right panel. Similar plots for the unit cell volume V and the volume strain ΔV are shown in Figure 4 in the left and the right panels, respectively. The c/a ratio, which is 1.8572 ± 0.0001 at $T = 296$ K, increases linearly with decreasing temperature down to the Néel temperature and then attains a constant value $c/a = 1.8643 \pm 0.0001$ at low temperatures. A closer inspection of the temperature variation of the lattice pa-

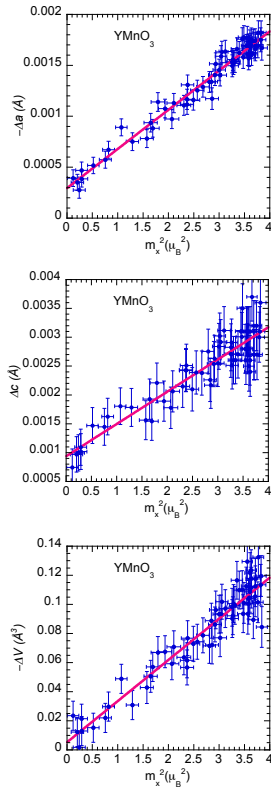


FIG. 6: (Color online) Linear plots of the lattice strains Δa , Δc and ΔV vs. the square of the ordered magnetic moment of the Mn ion in YMnO_3 .

rameters shows that the magnetoelastic effects become actually noticeable at temperatures substantially above $T_N \approx 70$ K. We can tentatively assign a temperature $T^* \approx 100$ K at which the magnetoelastic effect first becomes noticeable. The appearance of the magnetoelastic effect at temperature higher than T_N is presumably due to the short-range spin correlations. The spontaneous linear magnetostriction along the a -axis at $T = 0$ is $\Delta a/a_0 = -2.944 \times 10^{-4}$ and that along the c -axis is $\Delta c/c_0 = 2.633 \times 10^{-4}$. The spontaneous volume magnetostriction $\Delta V/V_0$ is -3.252×10^{-4} . Here a_0 , c_0 and V_0 are the extrapolated lattice parameters and the unit cell volumes at $T = 0$ for a fictitious non-magnetic solid obtained by the method described in the previous section. Note that although we determined $\Delta V/V_0 = -3.252 \times 10^{-4}$ by fitting the non-magnetic background and subtracting the experimentally determined unit cell volume, one can also calculate this from the relation $\Delta V/V_0 = 2\Delta a/a_0 + \Delta c/c_0$. The calculated value turns out to be $\Delta V/V_0 = -3.255 \times 10^{-4}$, very close to the value -3.252×10^{-4} determined semi-

independently. This indicates that the method we used for the determination of the non-magnetic background is reliable or at least consistent. One must however point out that the paramagnetic and fictitious non-magnetic background volumes are not really the same but we have assumed this to be the case for simplicity during the present analysis.

Figure 5 shows the temperature variation of the x -component of the ordered magnetic moment m_x of the Mn ion, obtained by fitting the measured Bragg intensities of the nuclear and magnetic reflections with the known crystal and magnetic structure models. The ordered magnetic moment decreases with increasing temperature and becomes zero at $T_N \approx 75$ K. We did not have enough data points close to T_N and therefore the critical exponent β could not be determined.

One expects that the spontaneous magnetostriction is proportional to the square of the ordered magnetic moment. This is at least the case for volume magnetostriction for a single sublattice ferromagnet²⁴. However our recent investigations^{25,26} on transition metal difluorides MF_2 ($M = \text{Mn, Co, Fe, Ni}$) showed that this is also the case for these simple antiferromagnets with the rutile structure. To check the coupling between the spontaneous magnetostriction and the ordered magnetic moment, or the order parameter of the antiferromagnetic phase transition in YMnO_3 , we plotted in Fig. 6 the lattice strains Δa , Δc and ΔV vs. the square of the x -component of the ordered magnetic moment of the Mn ion. The linear plots show that the lattice strains in YMnO_3 indeed couple to the square of the magnetic moment or the order parameter. This result also suggests that a second-order spin Hamiltonian is sufficient to describe the magnetic system of YMnO_3 . It is not necessary to invoke higher order spin Hamiltonian consisting of, for example, four-spin exchange for YMnO_3 .

IV. DISCUSSION AND CONCLUSIONS

Although we were successful in determining the magnetoelastic effects on the lattice parameters, our attempts to extract the temperature variation of the positional parameters of YMnO_3 below T_N did not succeed, presumably because of the $\mathbf{k} = 0$ magnetic structure of YMnO_3 . In such structures, magnetic reflections arise below T_N on the same positions as the reflections of structural origin. Well above T_N diffuse magnetic scattering is observed, becoming magnetic Bragg reflections below T_N . However, the magnetic scattering in general coincide with nuclear reflections. There are only a few pure magnetic reflections where structural reflections are not allowed due the space group extinctions. The least squares refinement of the crystal and magnetic structures using overlapping nuclear and magnetic intensities at the same reciprocal lattice positions has the problem of separating magnetic and nuclear intensities and therefore lead to correlations between the magnetic and structural pa-

rameters. Due to the correlations between structural and magnetic parameters, the positional parameters show abnormal deviations at and near T_N . Also these deviations are different if you come from the high or low temperature sides in a sequential refinement in which one uses the refined parameters of the previous data set as the start parameters of that for the next data set. One way to avoid such unwanted correlations is to use polarized neutron diffraction. The other useful method to disentangle the magnetic and structural parameters is to measure neutron diffraction intensities to a very high momentum transfer $Q = 4\pi \frac{\sin \theta}{\lambda}$. Our present data collected on a reactor based diffractometer at the thermal neutron beam are limited to about 7 \AA^{-1} only. Such high- Q diffraction data can be collected at a spallation neutron source. One can then refine the crystal structure using only the high- Q data and the magnetic structure using only the low- Q data. In this way one can hope to get the magnetoelastic effect on the positional parameters (bond distances, symmetric shifts etc.) as well and not just the lattice magnetoelastic effect that we determined in the present paper. Lee et al.²⁷ have obtained magnetoelastic effects of the structural parameters and bond distances of YMnO_3 , LuMnO_3 and $\text{Y}_{0.5}\text{Lu}_{0.5}\text{MnO}_3$ from their neutron and X-ray diffraction investigations but they have not explained how they have avoided such correlations between the structural and magnetic parameters. In the absence of such explanation it is difficult to accept the results given by these authors²⁷. It is extremely important to check the correlation matrix of the refined structural and magnetic parameters, especially in the case of

a $\mathbf{k} = 0$ magnetic structure, because the structural and magnetic intensities appear at the same reciprocal lattice points and least squares refinement process involves dividing the intensities into structural and magnetic parts rather arbitrarily. Only polarized neutron diffraction can separate the magnetic and structural contributions directly and the authors²⁷ did not use such a method. We also checked carefully the supplementary information of the paper in the on-line version. It contains a lot of other information but does not contain the crucial information about the correlation matrix of the least squares refinement.

In conclusion, we have investigated the spontaneous magnetoelastic effects or magnetostriction in multiferroic YMnO_3 by neutron powder diffraction. By subtracting the background thermal expansion for a nonmagnetic lattice from the measured thermal expansions we determined the lattice strains Δa , Δc and ΔV due to the magnetoelastic effects as a function of temperature. We have also determined the temperature variation of the ordered magnetic moment of Mn ion by fitting the measured Bragg intensities of the nuclear and magnetic reflections with the known crystal and magnetic structure models. Our results show that the lattice strain due to the spontaneous magnetostrictions in YMnO_3 couples with the square of the ordered magnetic moment or the square of the order parameter of the antiferromagnetic phase transition. This result also suggests that a second-order spin Hamiltonian is sufficient to describe the magnetic system of YMnO_3 .

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